BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (11), 3383—3384 (1975)

Structural Changes of Iron Oxides by Ball-Milling in Different Media

Yasuhiko UEHARA
Electron Tube Division, Hitachi Ltd., Hayano, Mobara, Chiba 297

(Received April 18, 1975)

Synopsis. γ-Fe$_2$O$_3$, Fe$_3$O$_4$, and α-Fe$_2$O$_3$ subjected to steel ball-milling in water changed into a spinel-type solid solution, while in polar organic media no remarkable changes occurred. In non-polar media, the γ-Fe$_2$O$_3$ and a part of the Fe$_3$O$_4$ were transformed into α-Fe$_2$O$_3$, although α-Fe$_2$O$_3$ remained unchanged. The diffraction lines of the resulting α-Fe$_2$O$_3$ broadened markedly.

γ-Fe$_2$O$_3$ is known to be transformed irreversibly into α-Fe$_2$O$_3$ by such treatments as applying high pressure and grinding mechanically.[1,2] The transformation proceeds *via* the reconstruction of close-packed oxygen ion layers together with the displacement of ferric ions located at the interstices between the oxygen ions.[3,4] The present paper describes the structural changes of γ-Fe$_2$O$_3$, Fe$_3$O$_4$, and α-Fe$_2$O$_3$ caused by the ball-milling in different liquid media in order to clarify the effect of the medium.

The structure of γ-Fe$_2$O$_3$ is an inverse spinel with a lattice parameter of 8.350 Å accompanied by a superstructure which has an ordered arrangement of cation vacancies and ferric ions in a ratio of 1: 3 at the octahedral sites. Fe$_3$O$_4$ is crystallographically isomorphous with γ-Fe$_2$O$_3$, having a lattice parameter (8.396 Å) slightly larger than that of γ-Fe$_2$O$_3$ (8.350 Å). Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ form a γ-Fe$_2$O$_3$–Fe$_3$O$_4$ solid solution; this can be expressed by $\square_{x/3}\mathrm{Fe}_{3-x/3}\mathrm{O}_4$, where $\square$ is the cation vacancy and x is the degree of oxidation. α-Fe$_2$O$_3$ has a corundum-type rhombohedral structure, its unit cell having the lattice parameters $a=5.427$ Å and $\alpha=55°17'$.

The γ-Fe$_2$O$_3$ used in this experiment showed a characteristic lattice parameter of 8.350 Å. The Fe$_3$O$_4$ used has the lattice parameter of 8.386 Å, indicating a slight oxidation of the stoichiometric Fe$_3$O$_4$. The particle shape of γ-Fe$_2$O$_3$ is rod-like approximately 0.8 μ in length and 0.2 μ in diameter. Both α-Fe$_2$O$_3$ and Fe$_3$O$_4$ are spherical particles about 0.3 μ in diameter. γ-Fe$_2$O$_3$, Fe$_3$O$_4$, and α-Fe$_2$O$_3$ powders were wet-milled in a steel ball mill having a capacity of 1.32 l. For each run, 30 g of the sample and 90 ml of the medium of extrapure grade were loaded into the ball mill. After milling at 90 rpm for 80 h, the resultant product was dried under reduced pressure and then examined by X-ray diffraction, using Mn-filtered FeK_α radiation. In order to compare the effect of different milling procedures, wet-milling in a porcelain ball mill and dry-grinding in an agate mortar were also carried out.

Table 1 shows the crystal structure, lattice parameter, and half-value width of each characteristic X-ray pattern of the products from γ-Fe$_2$O$_3$, Fe$_3$O$_4$, and α-Fe$_2$O$_3$ after 80 h of milling in the steel ball mill in the presence of different media. The structural changes occurred may be classified as follows:

1) In water, the spinel phase was stable and no significant line broadening of the X-ray diffraction lines was observed.

2) In polar organic media, neither structural changes nor line broadening was observed.

3) In a non-polar organic medium, the α-Fe$_2$O$_3$ phase was stable and nearly half of Fe$_3$O$_4$ was transformed into α-Fe$_2$O$_3$. However, a remarkable broadening of the diffraction patterns of both oxides was observed.

When γ-Fe$_2$O$_3$ was milled in the steel ball mill in the

TABLE 1. CHANGES IN CRYSTAL STRUCTURE, LATTICE PARAMETER, AND HALF-VALUE WIDTH OF EACH CHARACTERISTIC X-RAY PATTERN OF THE PRODUCTS FROM γ-Fe$_2$O$_3$, Fe$_3$O$_4$, AND α-Fe$_2$O$_3$ AFTER 80 hr OF MILLING IN THE STEEL BALL MILL IN DIFFERENT MEDIA

Medium		Dipole moment (D)	Starting material	Resultant product	Lattice parameter[b)] (Å)	Half-value width[c)] (degree)
Water		1.84	γ-Fe$_2$O$_3$	Spinel[a)]	8.371	0.30
			Fe$_3$O$_4$	Spinel[a)]	8.393	0.25
			α-Fe$_2$O$_3$	Spinel[a)]	8.371	0.30
Polar organic medium	Methyl alcohol	1.69	γ-Fe$_2$O$_3$	γ-Fe$_2$O$_3$	8.350	0.31
			Fe$_3$O$_4$	Fe$_3$O$_4$	8.386	0.26
			α-Fe$_2$O$_3$	α-Fe$_2$O$_3$	5.427	0.25
	Isopropyl alcohol	1.66	γ-Fe$_2$O$_3$	γ-Fe$_2$O$_3$	8.350	0.30
			Fe$_3$O$_4$	Fe$_3$O$_4$	8.386	0.24
			α-Fe$_2$O$_3$	α-Fe$_2$O$_3$	5.427	0.25
	Acetone	2.69	γ-Fe$_2$O$_3$	γ-Fe$_2$O$_3$	8.350	0.31
Non-polar organic medium	Cyclohexane	0	γ-Fe$_2$O$_3$	α-Fe$_2$O$_3$	5.43	1.2
			Fe$_3$O$_4$	α-Fe$_2$O$_3$+Fe$_3$O$_4$	5.43	1.0
			α-Fe$_2$O$_3$	α-Fe$_2$O$_3$	5.43	1.0

a) Spinel: γ-Fe$_2$O$_3$–Fe$_3$O$_4$ solid solution. b) Lattice parameters of starting materials. γ-Fe$_2$O$_3$: 8.350 Å, Fe$_3$O$_4$: 8.386 Å, α-Fe$_2$O$_3$: 5.427 Å. c) Half-value widths for starting materials. γ-Fe$_2$O$_3$ (311): 0.27°, Fe$_3$O$_4$ (311): 0.20°, α-Fe$_2$O$_3$ (422): 0.22°.

presence of water, the lattice parameter changed from 8.350 Å to 8.371 Å, the superstructure lines such as (210), (211), and (300) disappeared completely and the color changed from brown to black. These facts indicate that γ-Fe_2O_3 was reduced during the milling to give a γ-Fe_2O_3–Fe_3O_4 solid solution. Fe_3O_4 was also reduced to some extent to give Fe_3O_4 containing less oxygen than the original Fe_3O_4, accompanied with a change in the lattice parameter from 8.386 Å to 8.393 Å. α-Fe_2O_3 showed a complete transformation from the rhombohedral into the spinel structure with a lattice parameter of 8.371 Å which coincides with that of the milled γ-Fe_2O_3. Meanwhile, the color of α-Fe_2O_3 changed from red to black. However, when γ-Fe_2O_3, Fe_3O_4, and α-Fe_2O_3 were milled in a porcelain ball mill, no changes in the structure, lattice parameter, and color occurred. Therefore, it is likely that a mechano-chemical reaction is characteristic of the milling in the steel ball mill.

When γ-Fe_2O_3, Fe_3O_4, and α-Fe_2O_3 were milled in such polar organic media as methyl alcohol, isopropyl alcohol, and acetone, their structures, lattice parameters, and colors remained unchanged. The diffraction lines were as sharp as they were in the case of milling in water.

When milled in non-polar cyclohexane, γ-Fe_2O_3 was completely transformed into α-Fe_2O_3. In the case of Fe_3O_4, nearly half of the sample was transformed into α-Fe_2O_3; the diffraction lines of the resultant α-Fe_2O_3 were found to be remarkably broadened. Nearly identical results were obtained from an experiment by dry-grinding in an agate mortar.

During the milling, a microstrain concentrates in the lattice increasing the lattice distortion and the strain energy.[5] The increase in the lattice distortion results in the X-ray line broadening.[6] At the same time, the fresh surface produced by the milling is reactive with respect to the adsorption of polar molecules decreasing the surface energy and the fracture stress.[7] The fact that the X-ray diffraction lines remained as sharp as before can be explained, if one accepts that the adsorption of polar molecules decreases the fracture stress avoiding a remarkable increase in the microstrain concentration in the lattice. In the case of milling in non-polar media, on the other hand, the microstrain concentration increases gradually in the lattice and the X-ray diffraction lines become broader. In the case of milling in water, the sample is reduced to give a spinel phase containing less oxygen. In this reduction reaction during the milling, the mechano-chemical reaction between the sample, the water, and the fresh iron surfaces should be taken into consideration.

References

1) Y. Goto, *Japan J. Appl. Phys.*, **3**, 739 (1964).

2) M. Senna, S. Tojo, and H. Kubo, *Nippon Kagaku Zasshi*, **92**, 780 (1971).

3) S. Kachi, K. Momiyama and S. Shimizu, *J. Phys. Soc. Japan*, **18**, 106 (1963).

4) J. Hornstra, *J. Phys. Chem. Solids*, **15**, 311 (1960).

5) D. Lewis, D. O. Northwood, and R. C. Reeve, *J. Appl. Cryst.*, **2**, 156 (1969).

6) *e.g.*, A. R. Stokes and A. J. C. Wilson, *Proc. Phys. Soc.*, **56**, 174 (1944).

7) P. Rehbinder, *Z. Phys.*, **72**, 191 (1931).